Magnetic Phase Diagram for the Spinel Ferrite Series $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ and $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ as Determined by Mössbauer Spectroscopy

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Magnetic Phase Diagram for the Spinel Ferrite Series $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ and $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ as Determined by Mössbauer Spectroscopy

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Abstract. The spinel series $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ ($0.0 \leq x < 2.0$) (MFC) and $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ ($0.0 \leq x \leq 1.0$) (MZFC) are progressively diluted on the A-sites by non-magnetic Mg^{2+} and/or Zn^{2+} ions as x increases. The different magnetic states as a function of temperature and composition could be determined by Mössbauer spectroscopy in conjunction with high external magnetic fields. From the spectra it was derived that only for the spinel samples MFC with $x \leq 0.6$ and MZFC with $x \leq 0.1$ a pure ferrimagnetic behavior exists down to 4K. In the composition range $0.8 \leq x \leq 1.2$ for MFC and $0.2 \leq x \leq 0.7$ for MZFC a marked canting of the A- and B-site spins was observed below a characteristic temperature T_f indicating a re-entrant semi-spin-glass behavior. Finally, for the samples with $x > 1.2$ (ZFC) and $x > 0.7$ (MZFC) an incomplete alignment of the spins remained up to the paramagnetic transition temperature T_g pointing to pure semi-spin glasses. Together with the temperature dependence of the average magnetic hyperfine field the complete magnetic phase diagram could be derived.

1. INTRODUCTION

The peculiar magnetic properties of magnetically disordered compounds have drawn the attention of many researchers during the last two decades. Although the frozen random magnetism in the so-called spin glasses was first restricted to magnetically diluted alloys, it became soon clear that also insulating systems can exhibit disorder and frustration, which are the two main conditions for a spin-glass behavior. Among those insulating materials, spinel compounds are a fruitful subject of investigation because the spinel structure generally permits a good selective magnetic dilution on the different lattice sites [1, 2]. Moreover, if the spinels are of the ferrite type, ^{57}Fe Mössbauer spectroscopy (MS) has been proven to be a very useful tool in order to determine the various magnetic phases according to composition and temperature [2,3]. A typical example is the study of the spinel series $\text{Mg}_{1-x}\text{Fe}_{2-x}\text{Ti}_x\text{O}_4$, showing a spin-glass-like behavior in certain composition regions [3]. In fact, most of the spinel materials exhibit a so-called semi-spin-glass behavior, which means that they order ferrimagnetically in one direction and show disorder in the other directions [2, 4]. In this paper a Mössbauer study of the selectively diluted spinel series $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ ($0.0 \leq x < 2.0$) (MFC) and $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ ($0.0 \leq x \leq 1.0$) (MZFC) is reported, demonstrating similar spin-glass behavior.

2. EXPERIMENTAL

The spinel compounds have been synthesized by starting from intimately mixed oxides which were pressed into pellets and heated at 900°C in oxygen atmosphere. After milling and repressing the pellets were again heated at 1000°C. The latter procedure has been repeated until homogeneous products were obtained. From each series, slowly cooled (S) (1°C/4min) and quenched samples (Q) (after 3 hrs at 1200°C) were prepared. Standard X-ray diffraction (XRD) patterns were recorded in order to check the homogeneity and to determine the cation distribution with respect to Mg^{2+} . The cation distribution with respect to Fe^{3+} has been determined directly from external-field MS. The spectra were recorded with a conventional constant-acceleration spectrometer using a ^{57}Co source. Velocities were calibrated using a standard hematite absorber. External fields up to 6T were generated by a superconducting magnet. The spectra have been analysed taking hyperfine-field distributions and in some cases also the distribution of the canting angles into account [5].

3. RESULTS AND DISCUSSION

In order to study the influence of the magnetic dilution in the spinel series it is imperative to determine first the content of the magnetic species on both lattice sites in the two series as a function of the composition. The cation distribution with respect to Mg^{2+} and Fe^{3+} has been determined from the XRD intensities, assuming Zn^{2+} and Cr^{3+} to be only present on the tetrahedral (A) and octahedral (B) sites respectively. The distribution with respect to Fe^{3+} has been obtained directly from external-field MS. The degree of inversion for the different series, i.e. the amount of Fe^{3+} on the A sites, is displayed in Fig. 1. For MFC the values from XRD and MS agree relatively well, whereas for MZFC a strong deviation is observed. This is mainly attributed to an erroneous determination of the Fe^{3+} distribution from MS due to some part of the B-site Fe^{3+} exhibiting a 180° spin rotation, resulting in an apparent A-site contribution in the spectra [6]. Also the possibility of some amount of Zn^{2+} on the B-sites is not

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excluded, which can be inferred from the slight, but systematic difference between the values of MS and XRD for the MZFC samples with low Zn content ($x < 0.5$).

Figure 1: Inversion parameter determined from XRD (■) and external-field MS (□)

Mössbauer spectra of the two series MFC-S and MZFC-Q have been recorded in external fields up to 6T and at different temperatures. For the compositions $x \leq 0.6$ and $x \leq 0.1$ respectively, no $\Delta m_l = 0$ lines are visible in spectra down to 4K, indicating a collinear spin structure over the whole temperature region. For those compositions the antiferromagnetic A-B interaction predominates resulting in pure ferrimagnets. In the composition range $0.8 \leq x \leq 1.2$ (MFC-S) and $0.2 \leq x \leq 0.7$ (MZFC-Q), a marked spin canting is observed by the appearance of the $\Delta m_l = 0$ lines at low temperatures. Above a certain temperature T_f an apparent collinear ferrimagnetic structure was re-established up to the Curie temperature T_C . For compositions larger than $x > 1.2$ (MFC-S) and $x > 0.7$ (MZFC-Q) the spin canting is observed up to the paramagnetic transition temperature T_g .

The difference between an ordered canted spin structure and a so-called re-entrant spin glass can be readily observed from the temperature dependence of the hyperfine field, determined from the zero-field spectra. An ordered canted structure exhibits a smooth curve for the temperature dependence of the hyperfine field. On the other hand, a semi spin glass above the transition temperature T_f possesses only a steady component of the magnetization in one direction which results in a lower hyperfine field. In the re-entrant spin-glass region at lower temperatures the freezing of the magnetic moments yields the full value of the hyperfine field. The transition will therefore be characterized by a kink in the hyperfine-field curve. In Fig. 2, the temperature dependence of the mean hyperfine field is displayed for the MFC-S system, showing clearly the re-entrant semi-spin-glass transition temperatures for the various compositions.

Figure 2: Mean magnetic hyperfine field vs. temperature of sample MFC

Figure 3: Magnetic phase diagrams for the two spinel series (RSSG = re-entrant semi spin glass; SG = spin glass)

From the aforementioned results the magnetic phase diagrams for both systems can be determined as displayed in Fig. 3. They both consist globally of a ferrimagnetic, a paramagnetic, a re-entrant semi-spin-glass region and one with spin-glass-type properties. For the MFC system the phase diagram is not well defined for $x \geq 1.6$ because, due to the high Cr^{3+} content with strong B-B antiferromagnetic interactions, a more complicated magnetic behavior with clusters, similar to the Zn-Cr-Ga spinel system [7] can be expected at very low temperatures. Therefore more precise measurements in conjunction with other techniques are needed to unravel the magnetic behavior in that region.

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